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Title: Engineered Nano-scale Ceramic Supports for PEM Fuel Cells. Tech Team Meeting Presentaion

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Intended for: Fuel Cell Tech Team Meeting

Fuel Cell Tech Team Meeting

Engineered Nano-scale Ceramic Supports for PEM Fuel Cells

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August 15, 2012

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Fuel Cell Tech Team Meeting

Engineered Nano-scale Ceramic Supports for PEM Fuel Cells

Abstract

Catalyst support durability is currently a technical barrier for commercialization of polymer electrolyte membrane (PEM) fuel cells, especially for transportation applications. Degradation and corrosion of the conventional carbon supports leads to losses in active catalyst surface area and, consequently, reduced performance. As a result, the goal of this work is to develop support materials that interact strongly with Pt, yet sustain bulk-like catalytic activities with very highly dispersed particles. Ceramic materials that are prepared using conventional solid-state methods have large grain sizes and low surface areas that can only be minimally ameliorated through grinding and ball milling. Other synthesis routes to produce ceramic materials must be investigated and utilized in order to obtain desired surface areas.

In this work, several different synthesis methods are being utilized to prepare electronically conductive ceramic boride, nitride, and oxide materials with high surface areas and have the potential for use as PEMFC catalyst supports. Polymer-assisted deposition (PAD) and aerosol-through plasma (A-T-P) torch are among several methods used to obtain ceramic materials with surface areas that are equal to, or exceed Vulcan XC-72R supports. Cubic Mo-based ceramic phases have been prepared with average XRD-determined crystallite sizes as low as 1.6nm (from full profile, XRD fitting) and a BET surface area exceeding 200 m^2/g. Additionally, black, sub-stoichiometric TiO_{2-x}, have been prepared with an average crystallite size in the 4nm range and surface areas exceeding $250m^2/gr$. Pt disposition using an incipient wetness approach produced materials with activity for hydrogen redox reactions and ORR. Cyclic voltammetry data will be shown for a variety of potential Pt/ceramic catalysts. Initial experiments indicate enhanced Pt metal-support interactions as well. Plane wave periodic density functional calculations (VASP) are being used to predict the thermodynamic and activation barriers for fundamental electrode processes occurring at platinum surfaces supported on thin films of the ceramic support materials. The results of this work will be used in order to optimize support properties.

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Overview

- **Timeline**
  - Project start : September 2009
  - Project end : September 2013
  - Percent complete (as of May 2012) : 66%

- **Budget**
  - Total project funding:
    - DOE share $2,000,000
    - Cost Share: NA
  - Received FY11: $250K
  - Funding Received (anticipated) FY12: $500K

- **Technical Barriers Addressed**[2]

A. Durability (Pt sintering, corrosion loss, effects from load-cycling & high potential)

B. Cost (Better Pt utilization balanced by cost difference of new support)

C. Electrode Performance (Pt sintering, corrosion loss, and loss of ESA)

- **Partners**
  - LANL (Project Lead)
  - UNM
  - ORNL (no-cost partner)
  - Dr. Jonathan Phillips, NPS

2. (Multi-Year Research, Development and Demonstration Plan, Section 3.4.4 "Technical Challenges")
*From http://www1.eere.energy.gov/hydrogenandfuelcells/mypp/pdfs/fuel_cells.pdf

Relevance - Objectives

- Project Objective: Develop a ceramic *support* alternative to carbon supports for a polymer electrolyte fuel cell cathode.

- Ceramic support must:
  - have enhanced resistance to corrosion and Pt coalescence.
  - preserve positive attributes of carbon such as cost, surface area, and conductivity.
  - be compatible with present MEA architecture & preparation methods.

- Catalyst based on ceramic support must eventually have desired activity for ORR.

- Materials properties goals include:
  - possess desired surface area and electronic conductivity
  - foster high Pt utilization and exhibit enhanced Pt–support interaction
  - adequate corrosion resistance
  - synthesis method / procedure amenable to scale-up
  - reasonable synthesis costs

Collaborations / Distribution of Technical Personnel

Los Alamos NATIONAL LABORATORY

- Materials characterization: XRD, XRF and thermal analysis; Eric Brosha (PI)
- Electrochemical characterization, ink and MEA prep, PAD synthesis, Pt deposition, SEM, XRD, TGA; Lior Elbaz
- Support Modeling; Neil Henson
- Fuel Cell Testing; Tommy Rockward

The University of New Mexico

- Conductive aerosol derived supports; Aaron Roy, Alexey Serov and Timothy L. Ward with Plamen Atanassov

ornl

- TEM Characterization; Karren More

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- Naval Post Graduate School; Prof. Jonathan Phillips

Project Summary to Date

- Project start to YR 1.5 (50% of 2nd year funding front loaded in 1st year)
  - Materials/synthesis methods explored
  - A-T-P plasma torch (LANL), Polymer Assisted deposition (PAD, LANL), aerosol-derived conductive oxide supports (UNM)
  - Rare-earth hexaborides, moly-nitride, substoich titania, Sn-doped RuO_x
  - Series of Go/No-Go decisions; PAD selected (desired phases prepared)
- YR 2 (1/2 funding) – PAD process capable of preparing ceramic supports with crystallite sizes below 2nm in scale.
  - γ-Mo_2N and sub-stoichiometric titania prepared but with substantial carbon residue
  - Cubic Mo_2C easily prepared
  - Pt with high resistance to agglomeration and grain growth when Pt component added into support in the precursor stage of the PAD process: Pt agglomeration seen only if nitride or carbide support Pt is destroyed.
  - Modeling Pt energetics on defected Mo_2N_x surface indicated strong Pt-support interaction.
- YR 3 – ½ cell durability AST show impact of carbon residue on catalyst durability
  - Carbon-free Mo_2N and low carbon residual Mo_2C substantially more durable than commercial Pt/C.
  - Methods for MEA prep using ceramic supports will require optimization

Approach: From AMR Meeting FY12 Milestones…

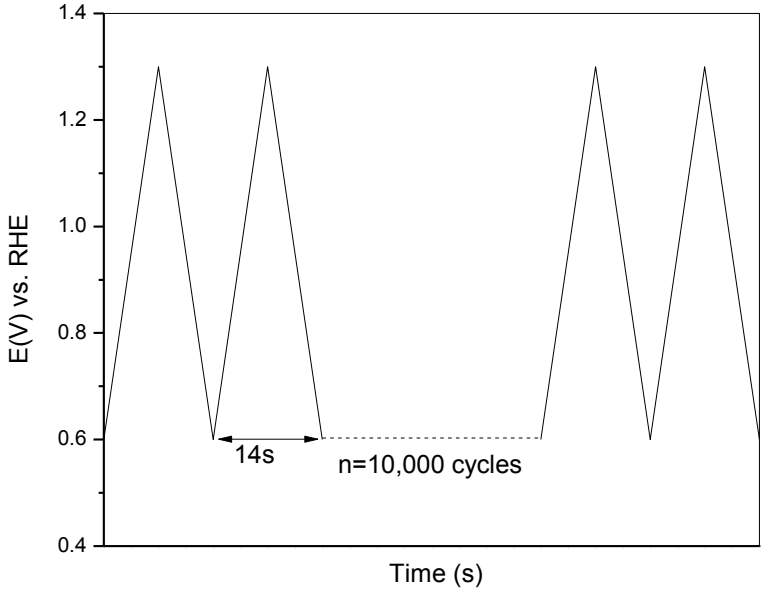
- As of Tech Team meeting date: project will meet 3rd year milestones and candidate materials have been identified with better durability than carbon.
  - Results from ½ cell AST durability testing (durability results in comparison to state-of-the-art commercial Pt/C catalysts) have lead to modifications in candidate materials selection and synthesis approaches.
  - YR 3 fuel cell testing show need for MEA optimization (4th yr), durability testing to compare with Pt/C.
- Identified and studied carbon residues inherent by-product of the PAD approach – 2011 AMR. Effect on durability studied (FY12).
  - Presence of carbon detrimental to catalyst durability.
- All Go/No-Go decisions for down-select of candidate materials scheduled in project have been made, though modified, since AMR based on latest data.
  - Mo-nitrides, Pt-imbedded Mo-carbides, and doped titanium oxides
- Emphasis this FY on electrochemical characterization and durability testing of support materials (on-going throughout remainder of project).
- Ink, MEA prep, and fuel cell testing with Mo_2C and titania supports began in FY12.
  - Mo-nitride fuel cell test can go ahead soon.

Today's Tech Team Meeting Presentation Outline

- Durability ½ cell testing, AST methodology and initial results using supports from project years 1 & 2
- Carbon-free Mo_2N synthesis routes (LANL & UNM)
- New Pt-embedded cubic phase Mo_2C prepared using Reactive Expansion Synthesis (RES) route at NPS
- Update on modeling work: TiO_{2-x} and energetics of Pt interactions with MoN and MoC surfaces
- Initial fuel cell testing results
- Summary
- FY 13 planned work

Technical Accomplishments and Progress FY12: Accelerated Stress Test (AST) Half Cell

Accelerated stress tests were conducted with the various ceramic supports in a half cell configuration to study their durability.



Conditions:

- Room temp. ~23°C
- Solution: de-aerated 0.1M $HClO_4$ in DI water
- Cycles: 10,000 between 0.6 and 1.3V vs. RHE
- ECSA meas. Every 1000 cycles (cycling between 0.0 and 1.2V vs. RHE)

Motivation:

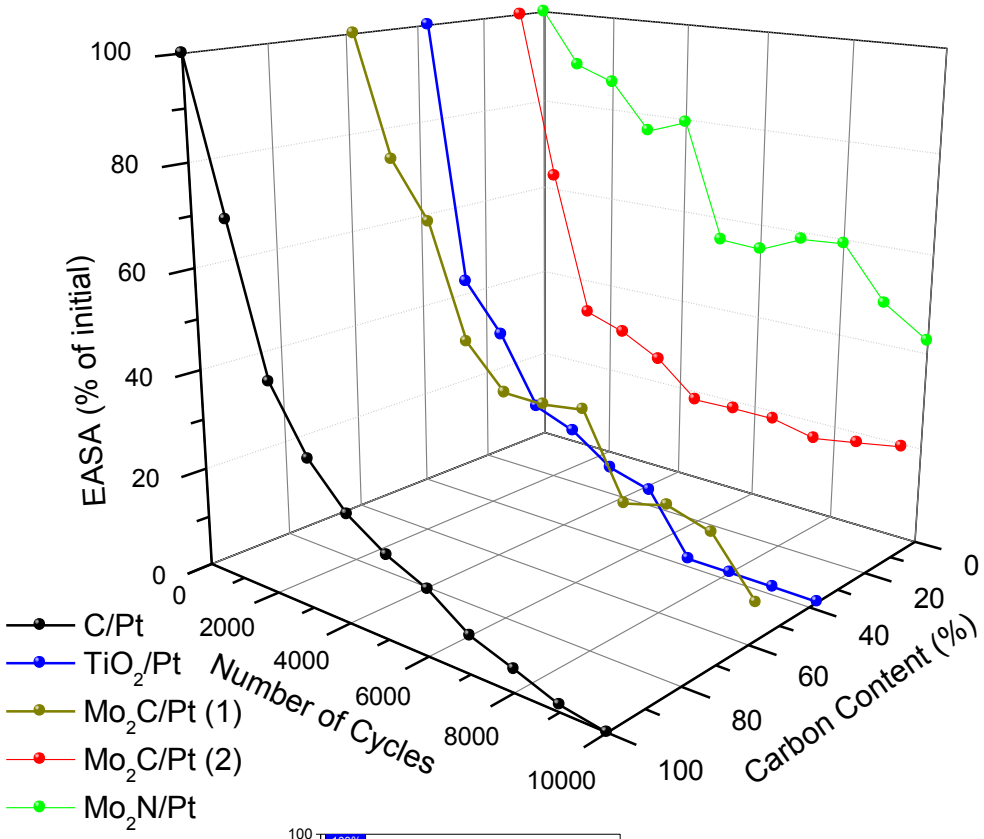
- The ceramic supports produced in this project should show superior stability when compared to common, state-of-the-art carbon supports.
- Half cell experiments allow to isolate the new support from other parameters which may interfere with the experiment (by keeping the number of variables as low as possible).

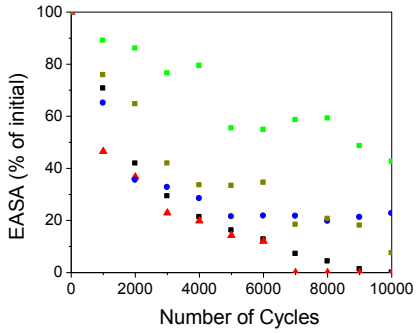
Supports studied

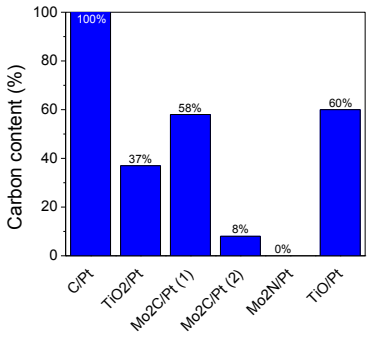
- **Pt/C** - Commercial Pt/C (ca. 47 wt% Pt loading)
- **TiO_2/Pt** - "Black" TiO_2/C prepared via PAD with 20 wt% Pt loading
- **Mo_2C/Pt (1)** - Cubic phase Mo_2C prepared via PAD with 20 wt% Pt Loading (58% residual C)
- **Mo_2C/Pt (2)** - Cubic Phase Mo_2C prepared via nitridation of ammonium molybdate/urea mixtures (8% residual C)
- **Mo_2N/Pt** - Cubic, γ-phase Mo_2N prepared using tradition solid state approach (0% residual C)

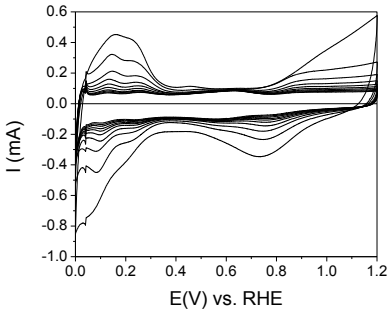
Technical Accomplishments and Progress FY12: Results of Initial AST

- AST's show that carbon supported catalysts loses it's activity after 10,000 cycles.
- There is a correlation between the amount of carbon content in the ceramic supports studied in this work and the loss of the activity.
- In order to make durable ceramic support for fuel cells we need to get rid of all carbon.
- Raises new challenges!



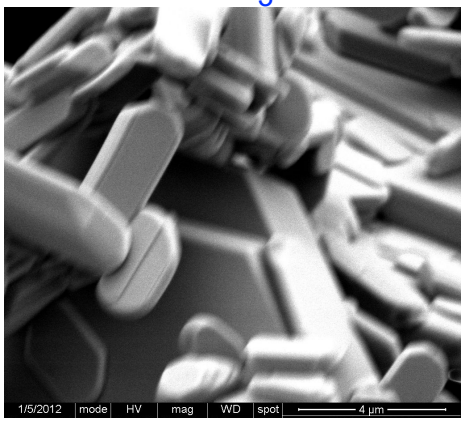


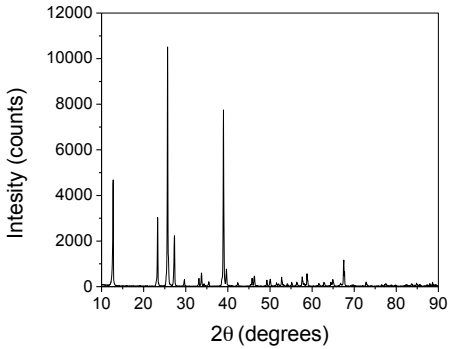




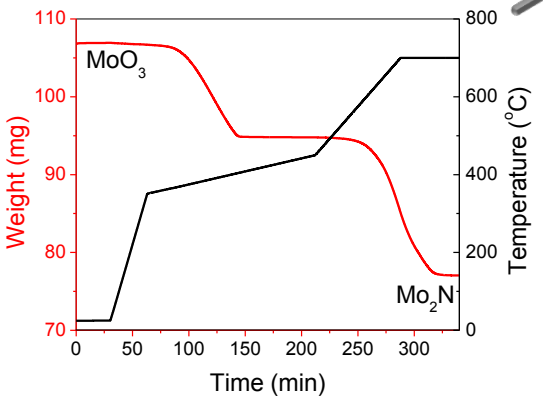
From AST Investigations, focus on carbon-free Mo_2N synthesis

MoO_3

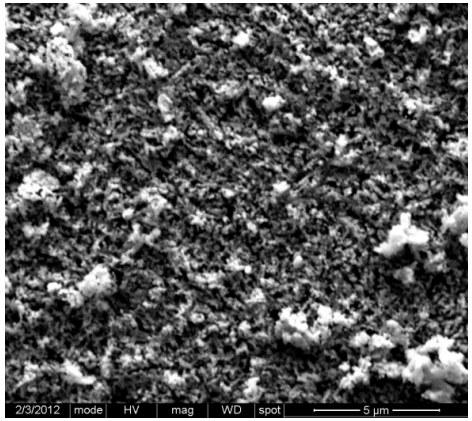


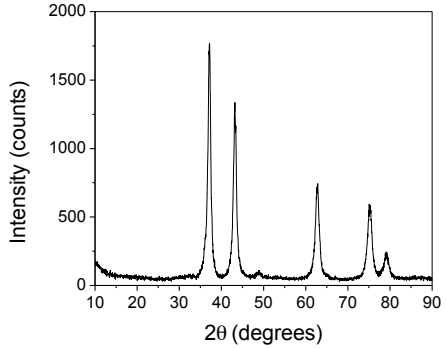


NH_3

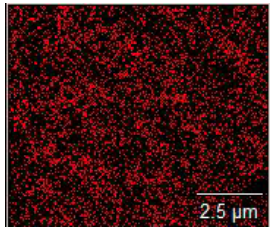


Mo_2N

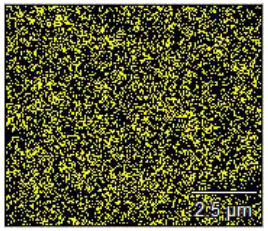




N



Mo



- Mo_2N/Pt was synthesized carbon free according to known recipes from literature.
- One inherent problem with the literature recipes is that the surface areas produced are inconsistent, vary wildly. Calls into question reliability and accuracy of BET measurements w/o standardized surface treatments!
- Still not entirely clear whether crystallite size of the Mo_2N is dependent on the crystallite size of the MoO_3 precursor.
- New thrust: the synthesis of nano-scale MoO_3 now being pursued via templated bulk and aerosol processes at UNM.

UNM Asked to Explore Non-Carbon Routes to Mo_2N

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Overview

- Poor progress toward high S.A. Mo-Oxide based on aerosol synthesis with surfactant templates
- Work highlighted at this year's 2012 AMR
- Change of direction toward use of inorganic sacrificial templates, which has given promising results
- Following review of UNM progress is focused on recent accomplishments using this approach

Bulk Synthesis by Sacrificial Inorganic Template

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Method (Bulk)

- High S.A. inorganic template impregnated with ammonium hepta-molybdate
- Air dried (+ air calcine if making oxide)
- Wash to etch template
- Post process in 5% NH_3 to convert to nitride
- Basic formulation is carbon free; porogens (if added) may contain carbon (e.g. urea)

Method (Aerosol)

- Dispersion of high S.A. template and ammonium molybdate aerosolized and passed through furnace with air carrier gas
- Wash to etch template (or wash after nitridation)
- Post process in 5% NH_3 to convert nitride

Bulk Mo-Nitride Synthesis by Sacrificial Inorganic Template

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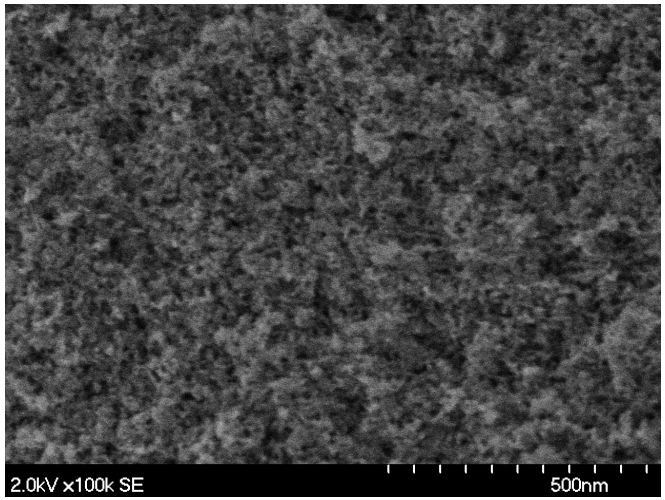
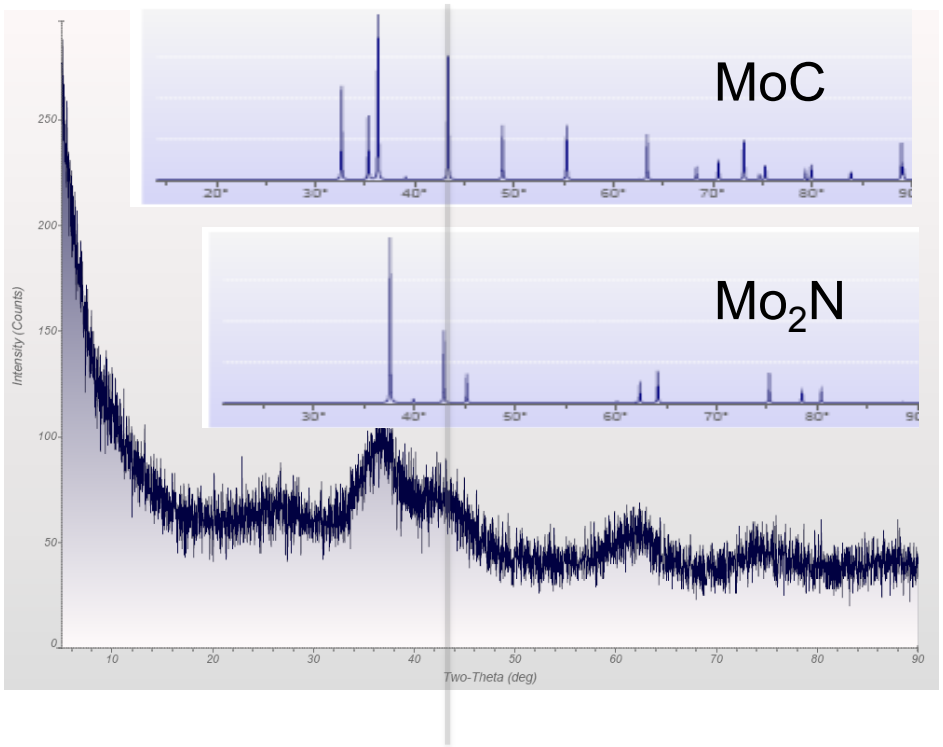
- Silica/urea/ammonium molybdate
- Calcination/Reduction: NH_3, 600°C, 2 hrs
- HF wash
- S.A. ~ 78 m^2/g





- Powder microstructure dictated primarily by sacrificial inorganic template
- Likely to have residual amorphous carbon from urea – need to do elemental analysis to confirm; exploring carbon-free porogens

Aerosol Mo-Nitride Synthesis by Sacrificial Inorganic Template

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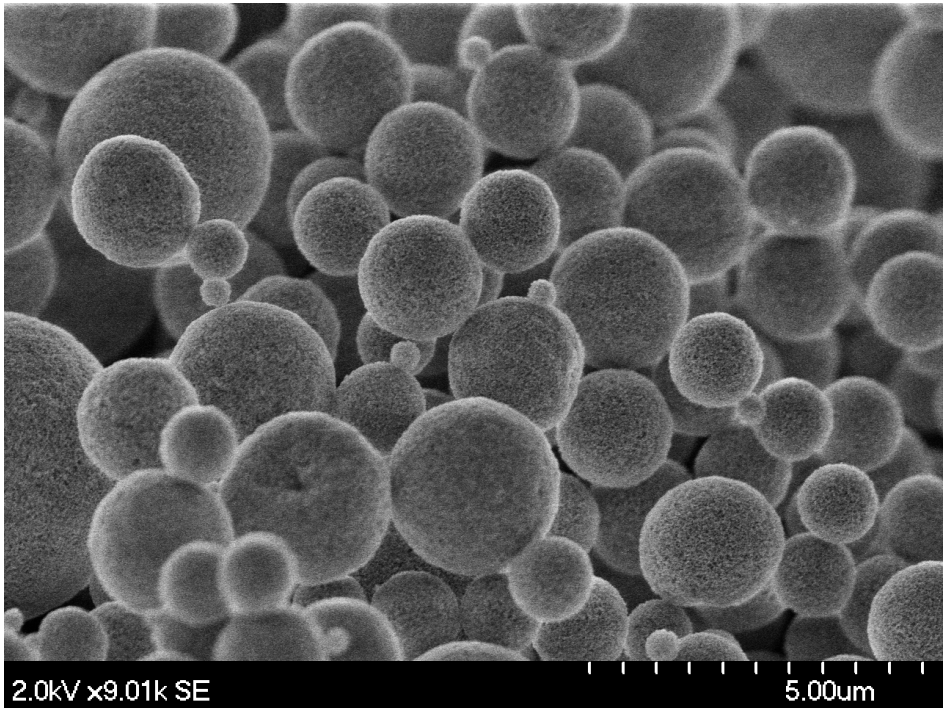
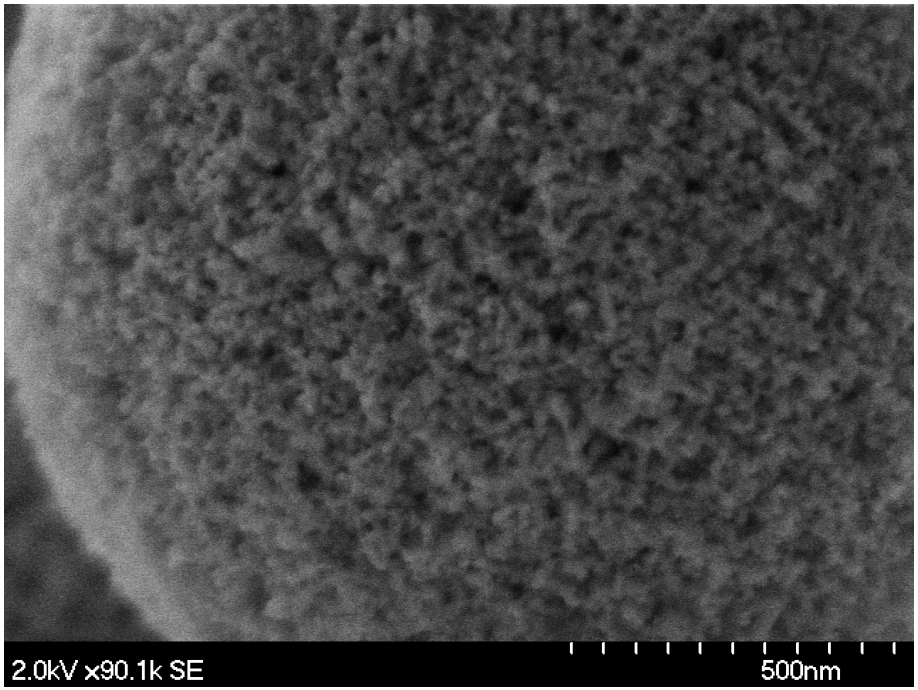
- AS-PRODUCED powder from aerosol synthesis
- silica/urea/ammonium molybdate
- Air, 300°C





- Particle morphology and size reflects typical aerosol pyrolysis product
- Particle microstructure dictated by sacrificial template and very similar to bulk synthesis powders

Aerosol Mo-Nitride Synthesis by Sacrificial Inorganic Template

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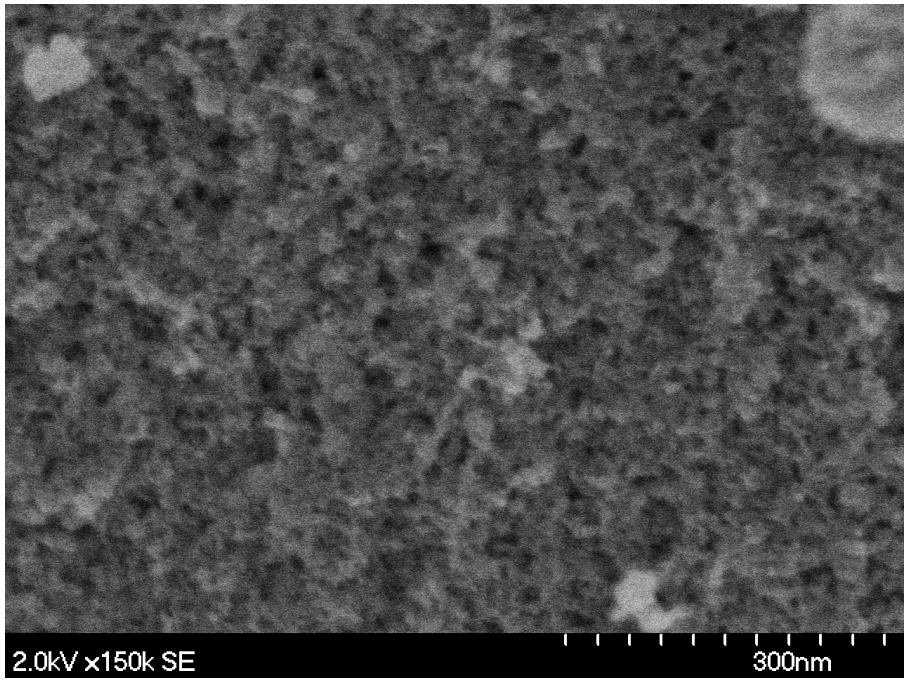
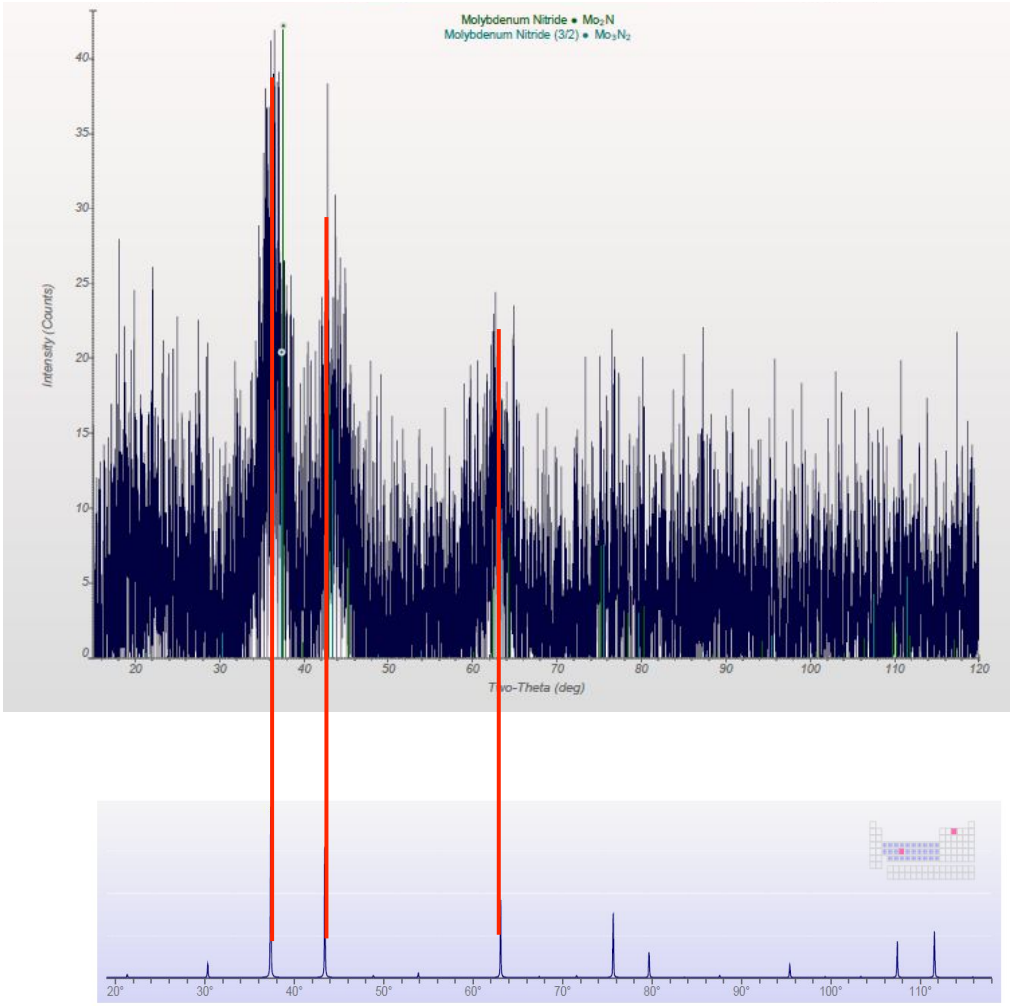
- AFTER POST-PROCESSING
- Calcined/reduced in 5% NH_3; 500°C; 2 hrs
- HF wash/etch (after calcination)
- S.A. ~ 40 m^2/g



- Lower S.A. than bulk synthesis has several possible causes – need to optimize/explore
- Microstructure appears unchanged – microstructure dictated by template, which is removed in post-processing
- Spherical particle morphology lost after calcination / reduction…need to understand better – this loss of morphology should be avoidable

Aerosol vs. Bulk Mo-Nitride Synthesis

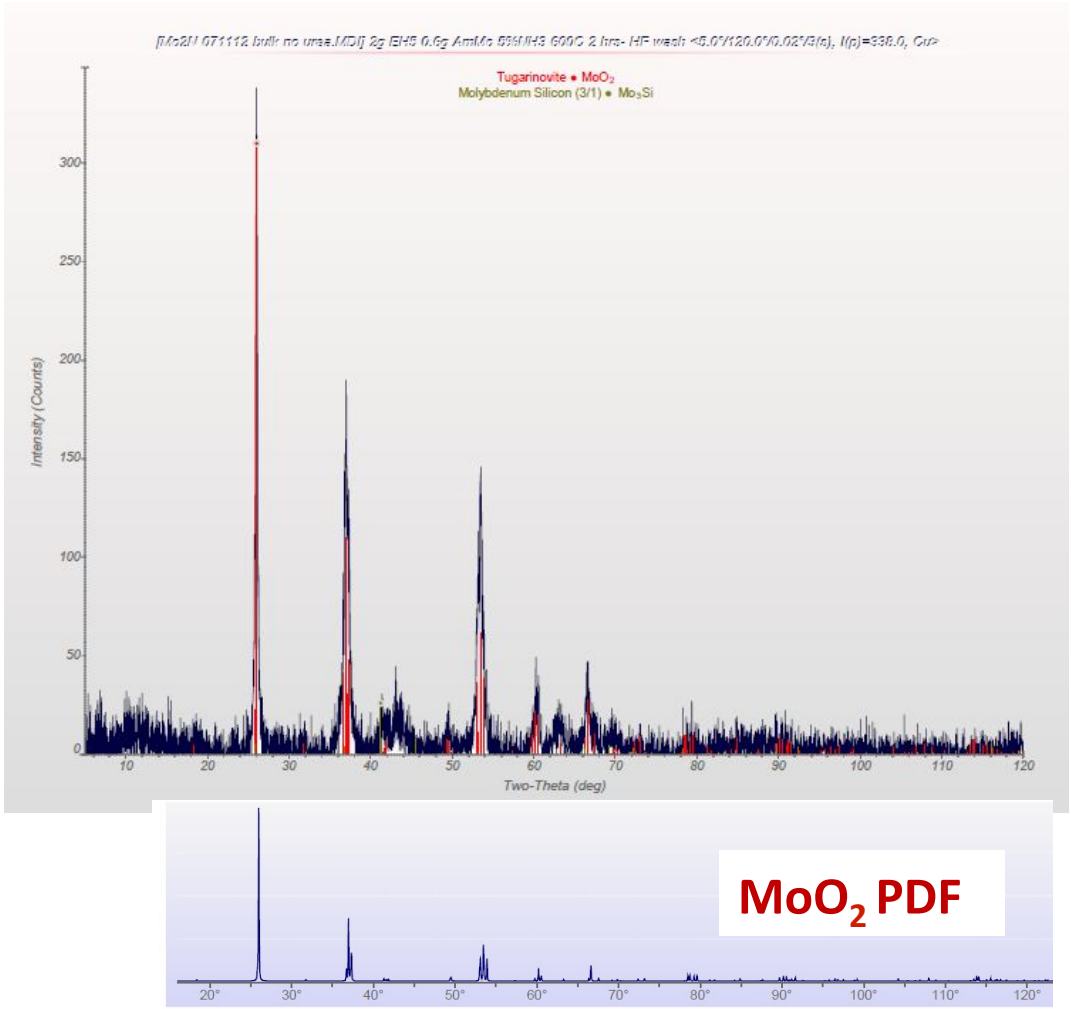


- Aerosol Synthesis: produced at 300 C in air, followed by post-processing in 5% NH_3 at 600°C for 2 hr
- Carbon free precursor
- XRD shows weakly crystalline Mo-N
- Same precursor formulation & treatment on bulk synthesis material gives Mo-oxide

- Aerosol synthesis provides benefits for nitridation - kinetics in post processing

Mo_3N_2 PDF

Aerosol vs. Bulk Mo-Nitride Synthesis



- Bulk Synthesis: air dried, followed by post-processing under 5% NH_3 at 600°C for 2 hrs
- Carbon free precursor
- XRD shows crystalline Mo-oxide
- Nitride conversion much slower than for aerosol-derived powder
- Same synthesis with urea in precursor led to nano-crystalline Mo Nitride/ Carbide (!)

Summary of Surface Areas from Sacrificial Inorganic Oxide Synthesis

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Bulk Synthesis

- Mo-Oxide using silica/urea/HF wash
  - 95 – 110 m^2/g
  - Question of residual silica
- Mo-Nitride using silica/urea/5% NH_3 treatment/HF wash
  - 78-88 m^2/g
  - Nano Mo-Nitride/Carbide by XRD
- Mo-Nitride using **carbon free** formulation (no urea)
  - 36 m^2/g
  - XRD shows crystalline MoO_2

- Question of residual silica in silica-templated materials (and effect on S.A.)
- Question of carbide/residual carbon in urea-containing formulations
- Carbon-free formulations give similar S.A. in aerosol material, lower S.A. in bulk

Aerosol Synthesis

- Mo-Oxide using silica/urea/air calcination / HF wash
  - Oxide not characterized for aerosol synthesis
- Mo-Nitride using silica/urea/5% NH_3 treatment/HF wash
  - 40 m^2/g
  - XRD not done
- Mo-Nitride using **carbon free** formulation
  - 44 m^2/g
  - XRD shows Mo_3N_2 (or Mo_2N?)

Summary Points – UNM Work

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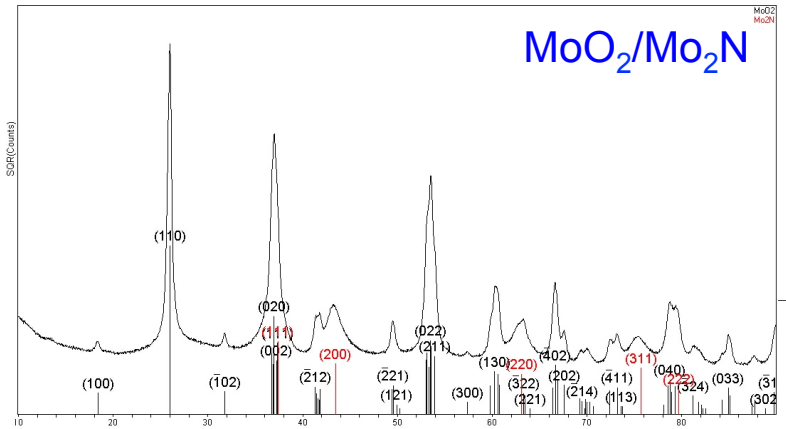
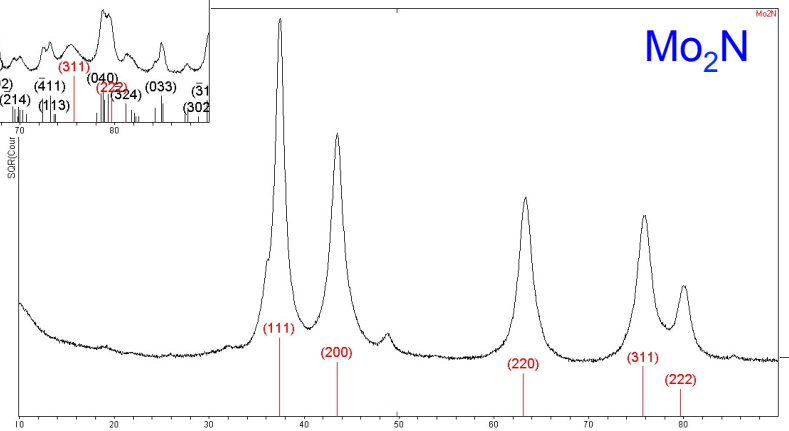
- Polymeric/surfactant templating approach has been redirected toward use of sacrificial inorganic templates (e.g., silica)
- Screening studies using bulk gelation, drying and calcination can be translated readily onto the aerosol synthesis platform
- Currently producing nanocrystalline MoN powders with aerosol-derived powders post-processed under 5% NH_3 with ~40 m^2/g
- Aerosol powders apparently have significant advantage in nitride formation kinetics compared to bulk for carbon free formulations
- Urea in the bulk synthesis apparently interferes with oxide network formation in the gelling/ drying stage – does not have same effect in aerosol synthesis
- Still not achieving the surface areas that are desired
- Exploring conditions, other templates and porogens to optimize
- Need more materials characterization (adsorption, N/C elemental analysis, etc.), as well as conductivity and electrochemical

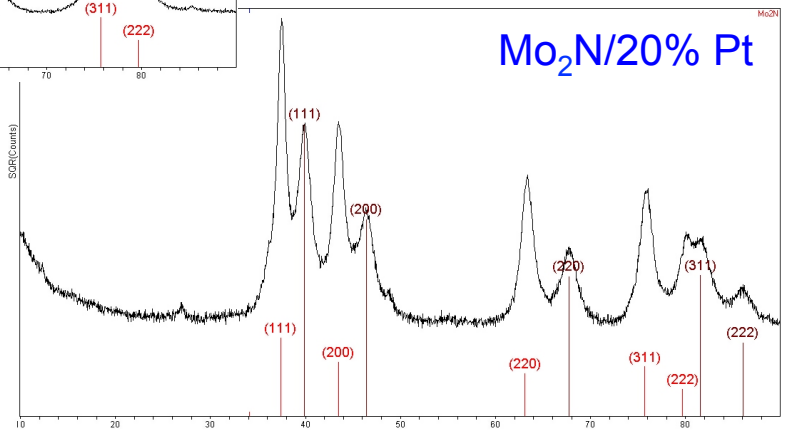
Further treatment of UNM aerosols and Pt deposition – LANL Work



NH_3 @ 700°C



Pt (incipient wetness)



- Further treatment of aerosols under pure ammonia turned the excess MoO_2 into Mo_2N.
- Final Mo_2N crystallite size: 7 nm
- Pt deposited on Mo_2N using incipient wetness gives 4 nm crystallites

Reduction Expansion Synthesis (RES): New Method for Rapid Fabrication of Highly Dispersed Supported Metal Catalysts

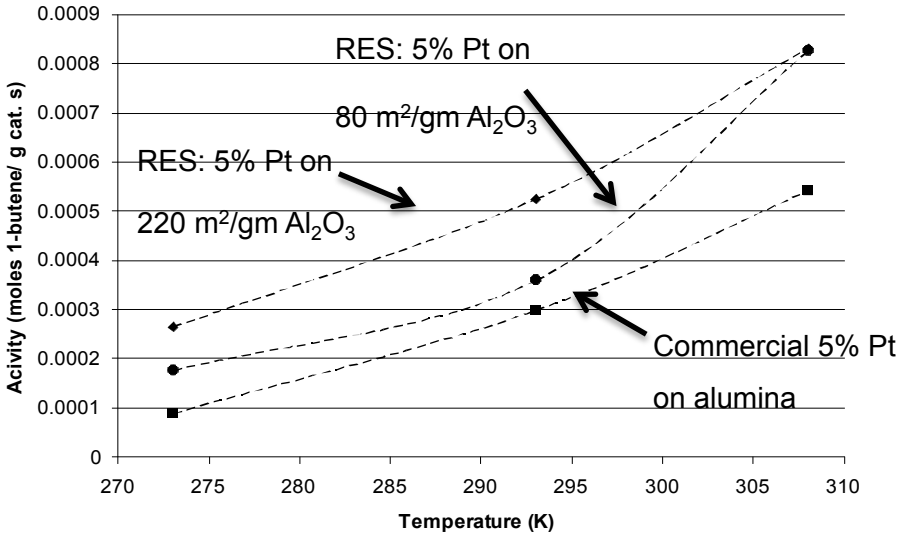
NAVAL POSTGRADUATE SCHOOL

Prof. Jonathan Phillips, NPS; jphillip@nps.edu

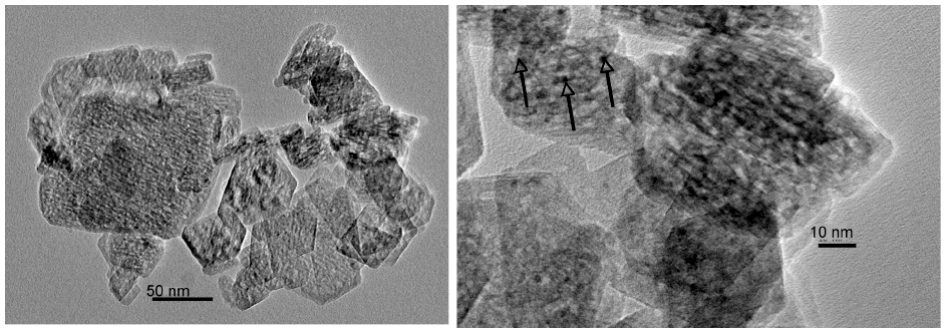
I. Superior activity

Activity for 1 butene hydroisomerization measured in a differential reactor.

Note: Both RES catalysts superior to commercial catalyst.



II. Particles sub 1 nm even at 5% Pt loading



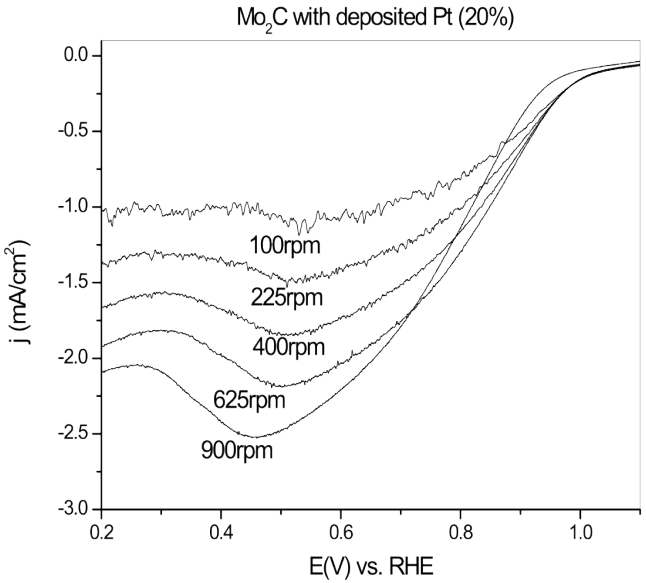
TEM images of 5 wt%Pt/ γ-Al_2O_3. LEFT- No particles are apparent on this scale. RIGHT- At this scale there are areas of high adsorption (e.g. at end of arrows) that are probably particles. These particles are of the order of 1 nm across.

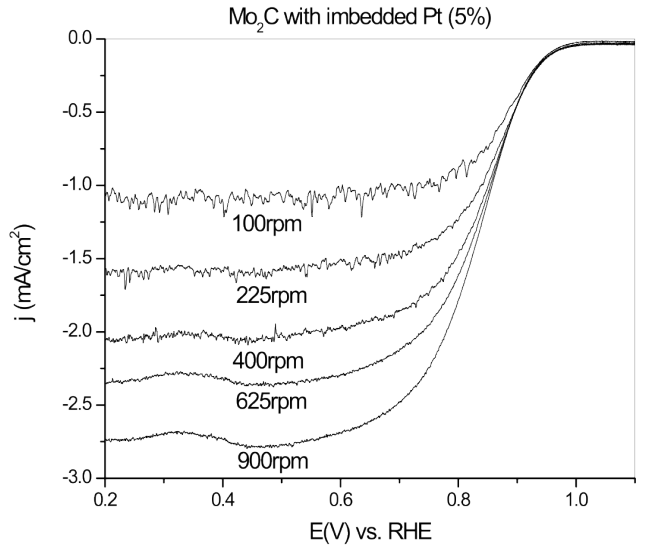
III. RES production of supported metal catalysts

Viable for standard catalytic processes and for fuel cells. The process for making them is: i) remarkably simple (physical mixing followed by heating for < 300 seconds at 800°C), ii) easily scaled, and iii) requires 'ordinary' and inexpensive equipment. Patents pending.

Catalysis of Oxygen Reduction Reaction Platinized Cubic Phase Mo_2C

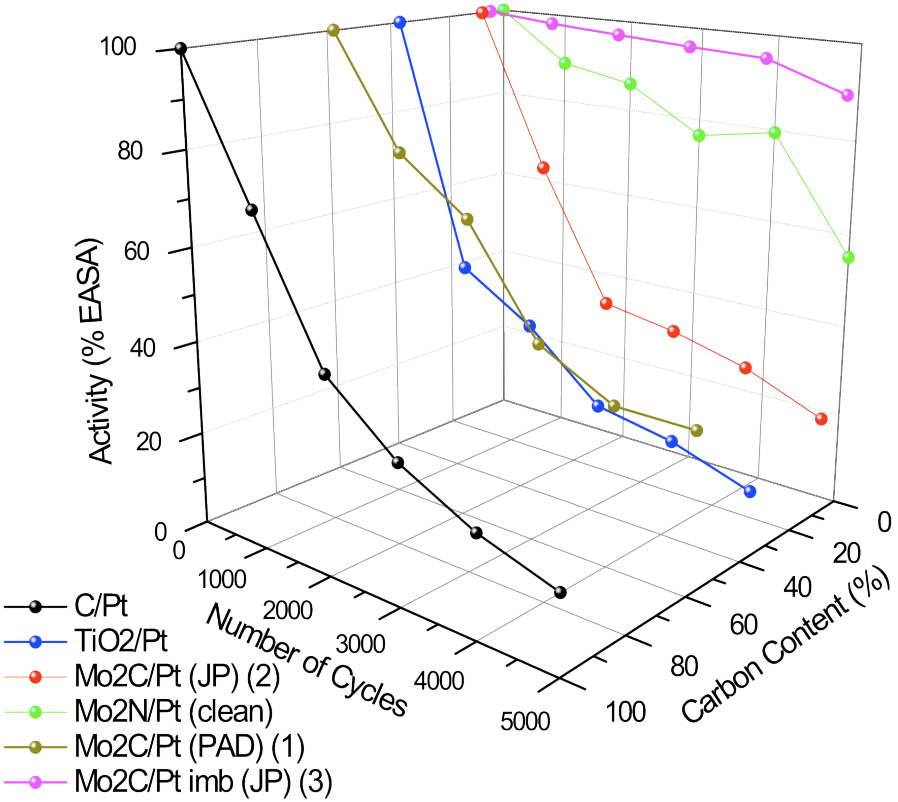
- Two samples investigated
  - 20 wt% Pt deposited on Mo_2C
  - 5 wt% imbedded Pt during RES synthesis
- RRDE measurements shows imbedded Pt sample superior activity to that of deposited Pt at much lower loadings. In both cases, no peroxide detected.
- ½ -wave potentials measured:
  - Imbedded Pt: $E_{½}$ = 0.88V vs. RHE
  - Deposited Pt: $E_{½}$ = 0.85V vs. RHE
- Mo_2C imbedded with 5% Pt shows high mass activity @ 0.9V vs. RHE when compared to Pt/C (ETEK); 74 vs. 40 A/g_{Pt}
- Experimental conditions:
  - Electrolyte: 0.1 M $HClO_4$
  - Gas: solution was saturated with O_2
  - Catalyst loadings: 24µg & 6µg Pt/cm^2
  - Scan rate: 5 mV/s

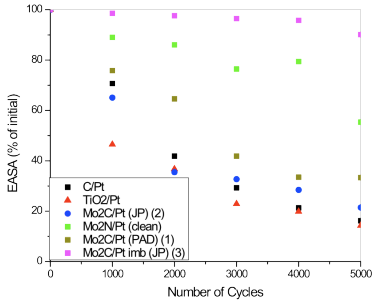


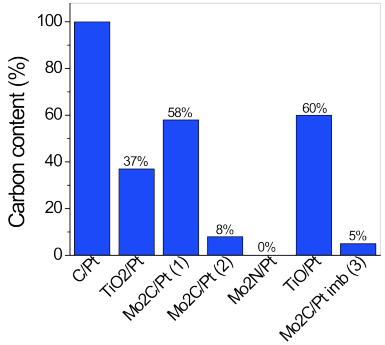


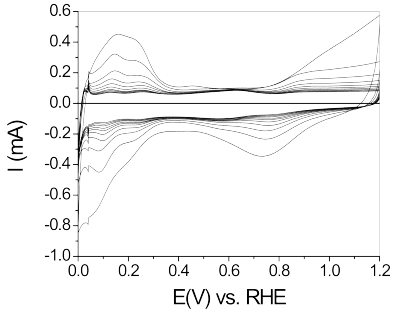
AST Results, RES-prepared Mo_2C with imbedded Pt

- RES-prepared Mo_2C, 5 wt % Pt imbedded compared to other supports
- AST conducted over 5000 cycles shows higher durability than previous supports
- Est. 5 wt% residual C (most likely left over from urea additives)
- Samples sent to ORNL for TEM characterization.
  - Surface or imbedded Pt ? Both?



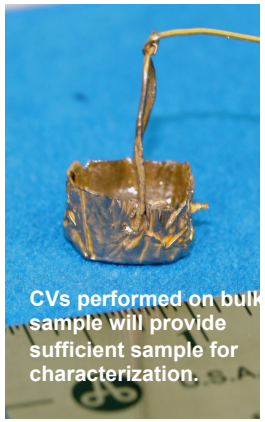


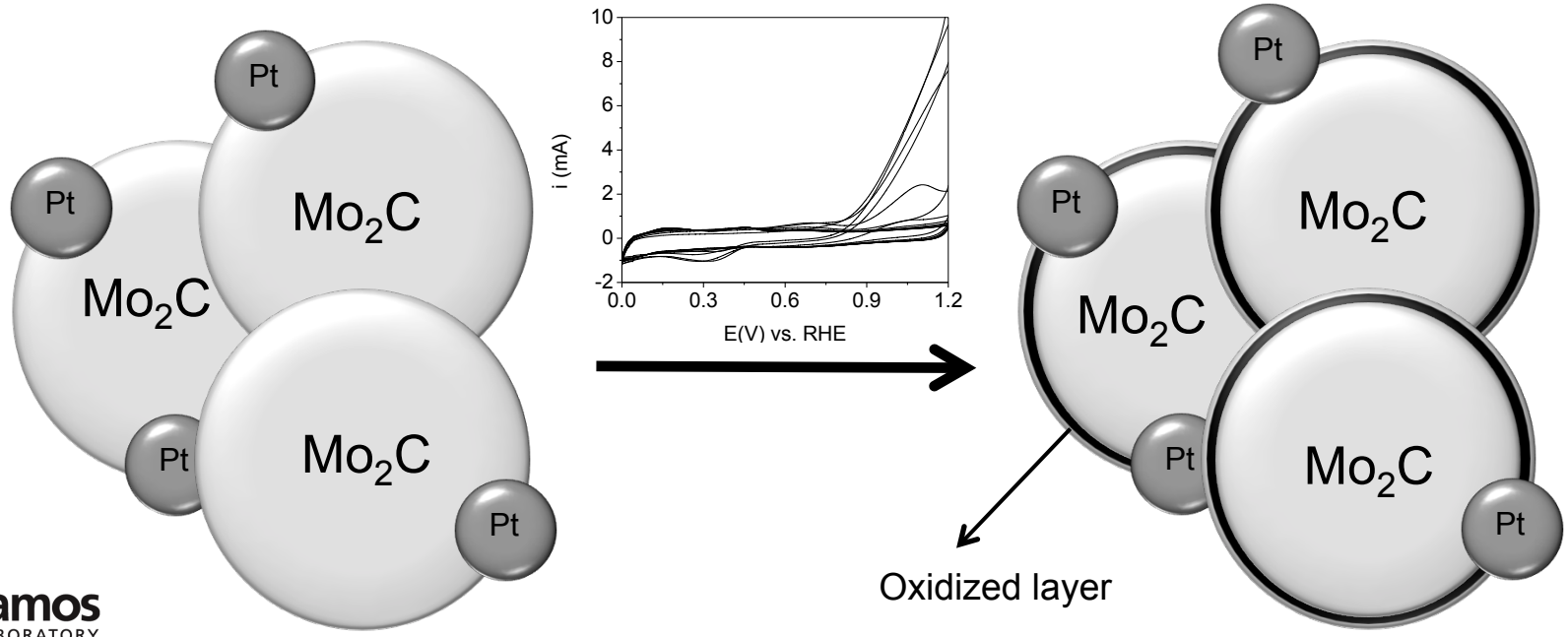




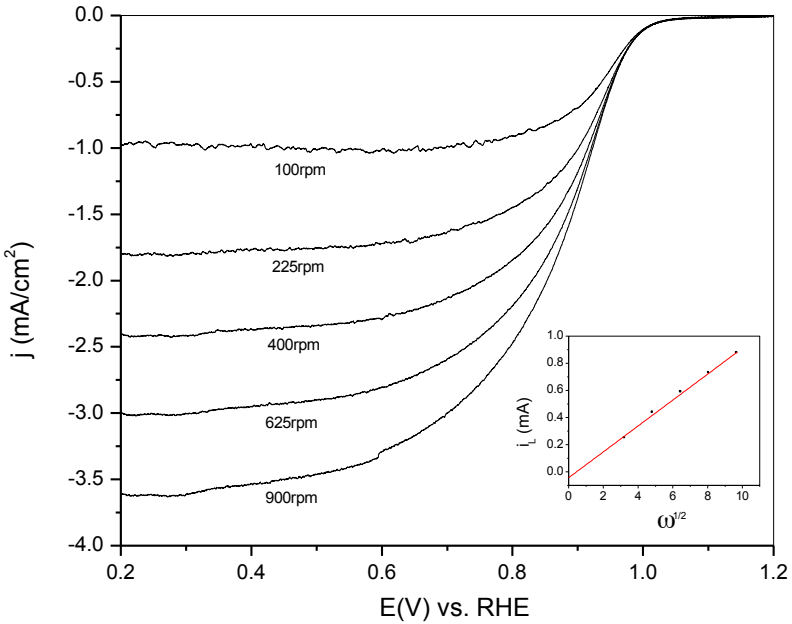
Surface oxidation of non-oxide ceramic supports

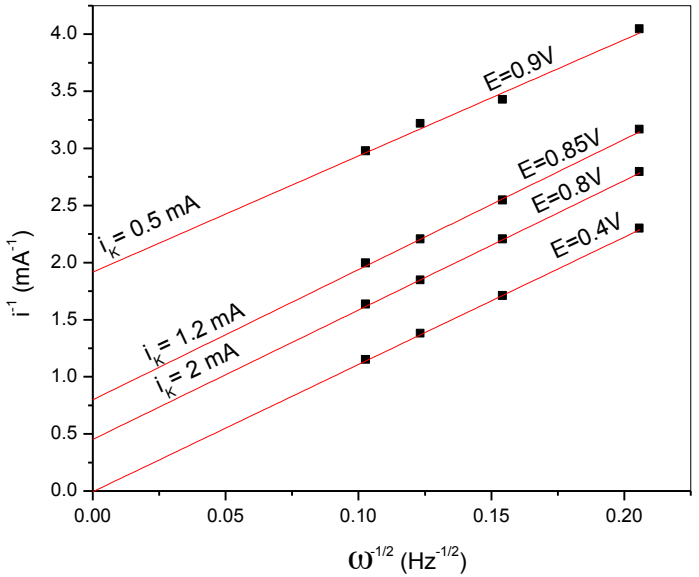
- Prior to AST's the supports are cycled for ~100 times (0-1.2V vs. RHE @ 100mv/s) until reaching a steady state.
- The non-oxide ceramic supports developed in this work show an oxidation process going on during this pre-treatment. This oxidation is presumed to form a thin oxidized layer on the surface of the support, thus passivating it.
- The support does not seem to lose its electronic conductivity since the surface at the point-of-contact of the support particles is not oxidize nor the core of the particles.
- This phenomena is under study with large quantities of support material in order to enable the characterization of the ceramic supports and to better understand the corrosion mechanism that occurs on their surfaces using different techniques.





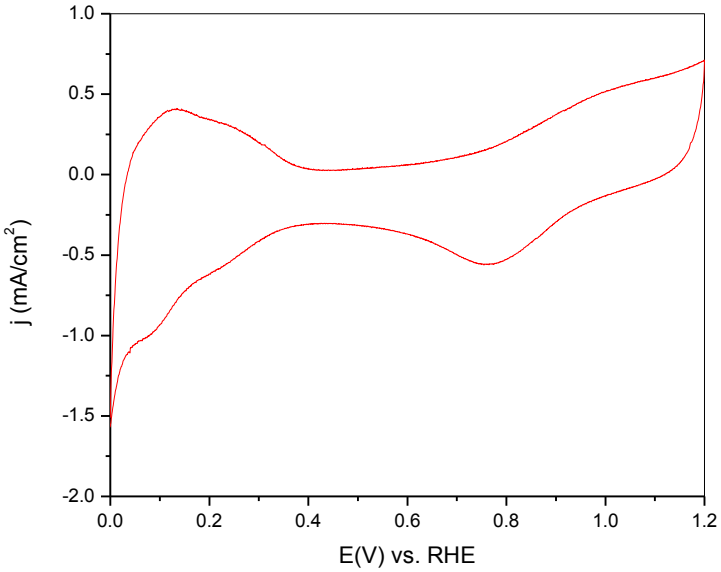
Technical Accomplishments and Progress FY12: 20%Pt/TiO_2(PAD)





- Conditions:
- Catalyst loading: 24μg Pt/cm^2
- RRDE: 0.1M $HClO_4$; scan rate 5mV/s
- CV: 0.1M $HClO_4$; scan rate 100mV/s

- Results:
- Half wave potential: $E_{1/2}$=0.94V vs. RHE
- Kinetic current @0.8V : i_K= 2mA
- Mass activity @0.9V: 84A/g_{Pt}
- Number of electron (form Levich) = 4.0 e$^-$
- EASA = 57.5 m^2/g_{Pt}

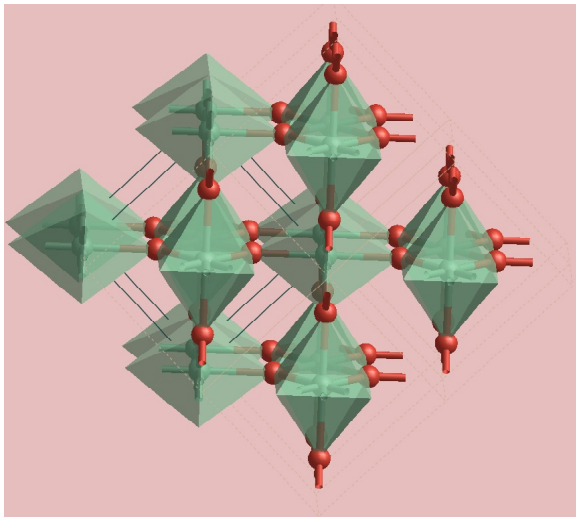


Computational Studies of Adhesion Energetics of Platinum to Ti_4O_7 phase of Titanium Oxide

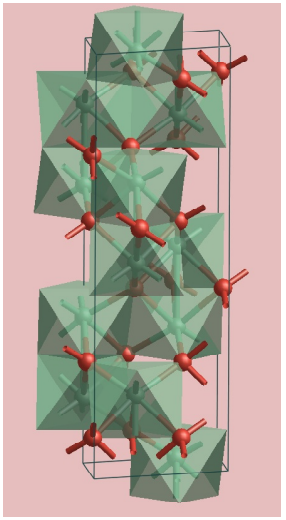
- Aim:
  - Calculations to predict thermodynamics of platinum binding to Magnéli phases of titanium oxide to assess stability of ceramic supports

- Approach:
  - Calculations to be performed using plane wave periodic density functional theory calculations (VASP software)
  - Build model for Ti_4O_7 phase
  - Based on these, build models for dominant surfaces
  - Determine most favorable binding sites for single and multiple platinum atoms on surfaces

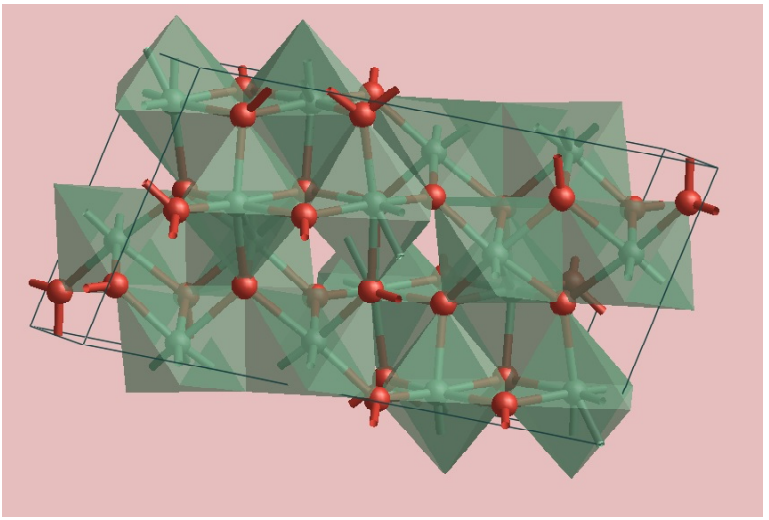
Models for Magnéli phases, Ti_nO_{2n-1}



TiO_2 rutile



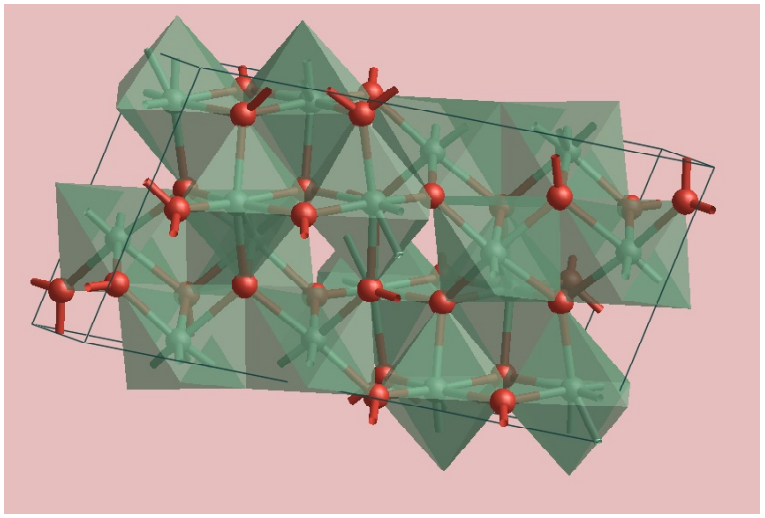
Ti_2O_3



Ti_4O_7

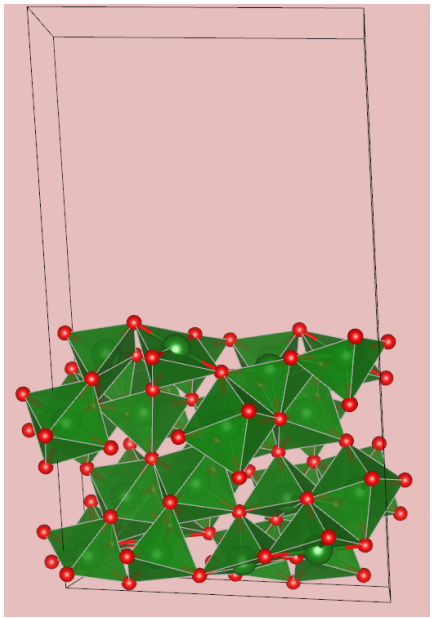
- Midway between TiO_2 and Ti_2O_3 structures
- Magnéli phases: regions of normal rutile structure with TiO_6 octahedra separated by crystallographic shear planes → unique surface structures
- Oxygen defects confined to planes
- 1st member of series, Ti_4O_7 is best characterized

Surface models for Ti_4O_7

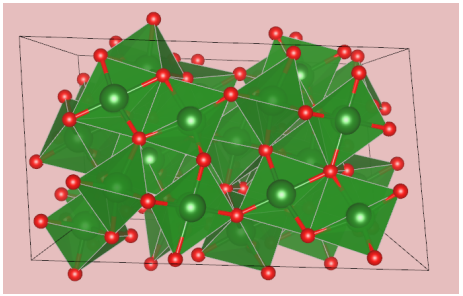


bulk

<100> side view



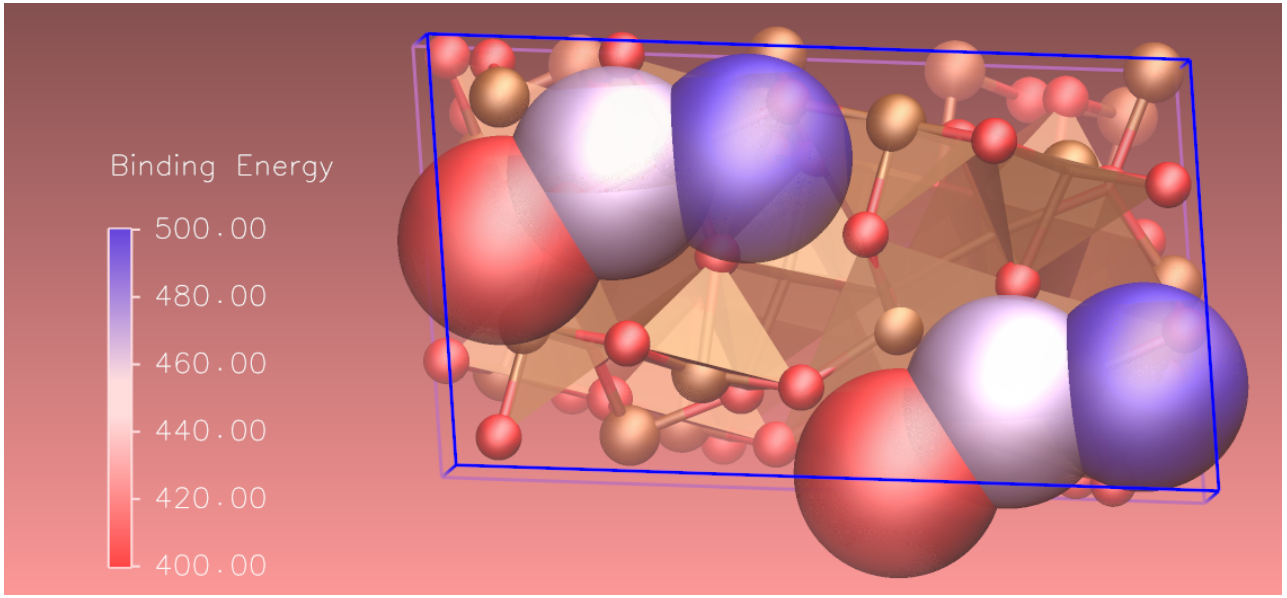
<100> top view



	a	b	c	α	β	γ
experiment	11.19	7.13	12.46	95.0	95.2	108.7
calculated	11.29	7.20	12.54	95.2	95.6	108.9

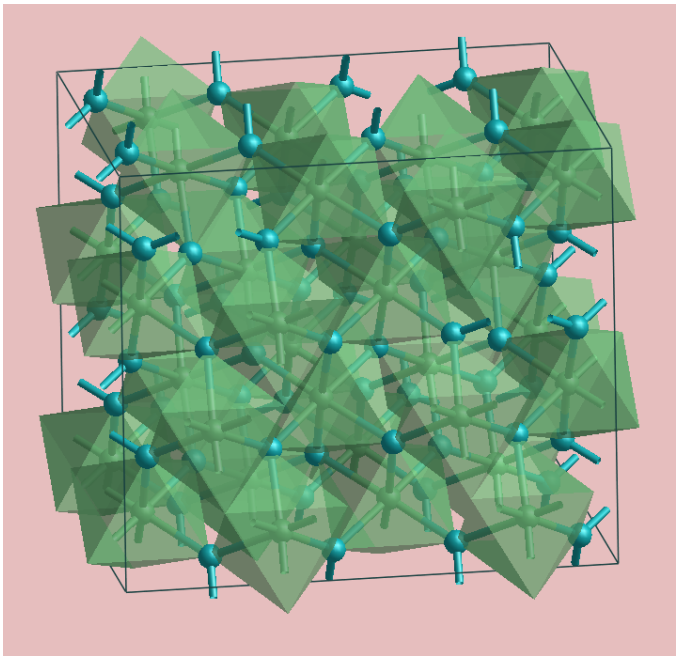
calibration: good reproduction of experimental bulk structure

Calculated binding energies for Pt on <100> Ti_4O_7

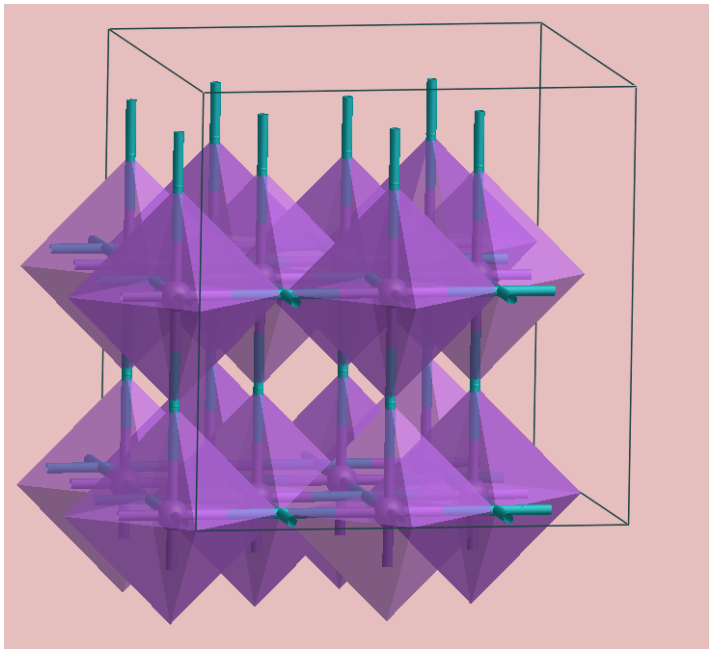


- Looking down on <100> surface
- Spheres are calculated binding sites for platinum on surface
- Oxygen defects confined to planes colored coded by binding energy in $kJmol^{-1}$
- Three sites related by symmetry of the surface, each less strongly bound than for Pt on Pt<111> (~ 630 $kJmol^{-1}$)
- Similar bonding energies for other low index surfaces

New: Comparison of Mo_2C and Mo_2N - Pt adhesion energies



α-Mo_2C orthorhombic



γ-Mo_2N tetragonal

- Average Pt binding energies similar for both structures on <100> surface
- Pt adhesion slightly stronger than for Pt on Pt<111>

Physics and Chemistry of Materials

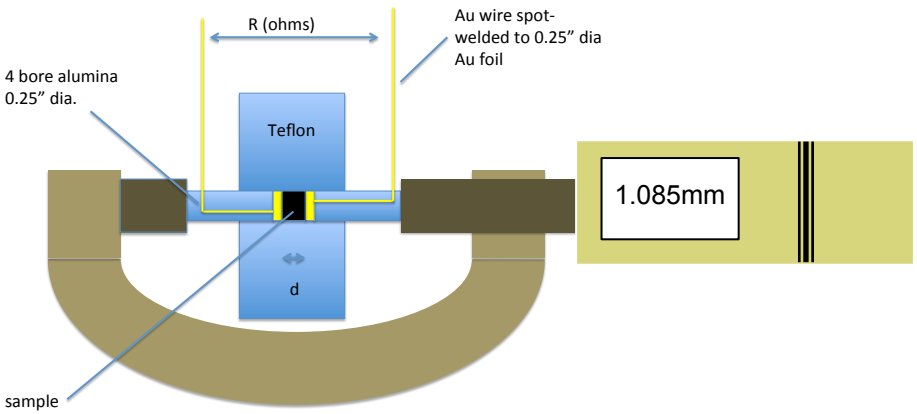
Shift Focus of Titania Oxide Support Work

- Unable to directly synthesize Ti_4O_7 phase using PAD process
  - TiO_2 and TiO prepared with nano-scale crystallites.
  - Activity and durability data obtained for PAD-prepared/platinized supports.
  - Prerequisite conductivity (for anatase) obtained by carbon residue.
  - Showed carbon negatively impacts durability.
  - Still have option of brute force reduction but at expense of sintering.
- Since this project began, Ti_4O_7 stability in question.
- Calculated binding energies, taken together with synthetic difficulties call into question how much effort should be invested pursuing this candidate.
- Decision made to study transition metal or rare-earth substituted TiO_2.
  - PAD process okay: oxidizing synthesis conditions mean no carbon residue.
  - Produce nano-scale crystallites derived from PAD but conductivity derived from chemical substitution.
  - Modified PAD process to prepare $Nb_xTi_{1-x}O_{2-x}$ (x=0.05, 0.1, and 0.2)

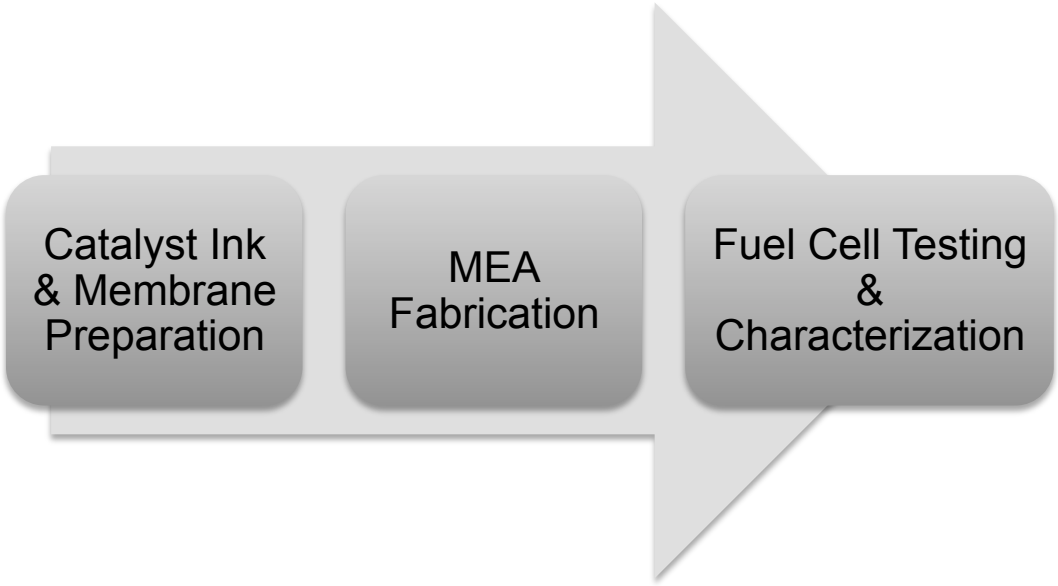
2-pt Support Resistivity Measurements

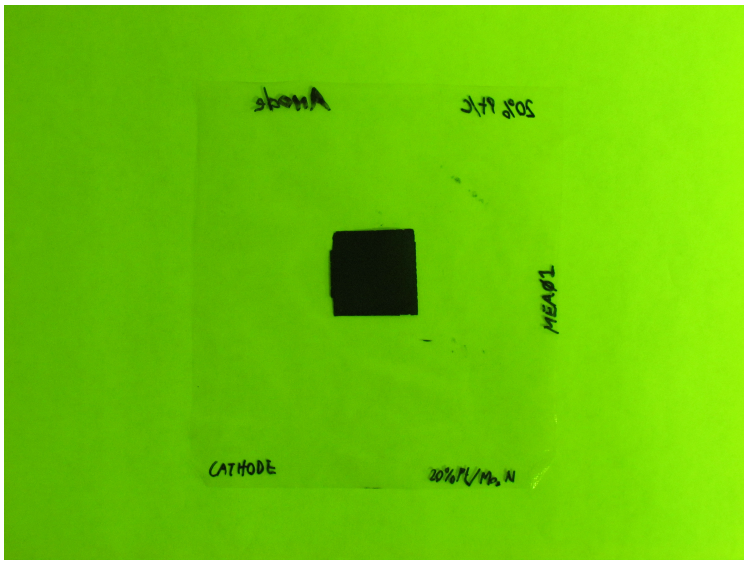
- Measurements of support resistivity have been made since project began.
- Data are always presented compared to Vulcan XC-72R for the same measurement.
- Better, more precise measurement method adopted last year.
- Quick screening possible.
- Still requires a certain minimum amount of sample that precludes tracking changes in resistivity with cell durability experiments.
- Ideal for samples recovered from Au-boat bulk CV experiment to be performed in near future.

Sample	ρ (ohm•cm)
$Mo_2C/5Pt_{em}$ (RES)	0.27
Mo_2C (RES)	0.18
$Mo_2N_{(TGA)}$ 90b	0.27
$Mo_2N_{(TGA)}$ 82c	0.35
UNM –B-MoO_2/MoN	0.47
UNM –B-Mo_2N_{1-x}	0.43
Vulcan XC-72R	0.60



Technical Accomplishments and Progress FY12: Fuel Cell Testing



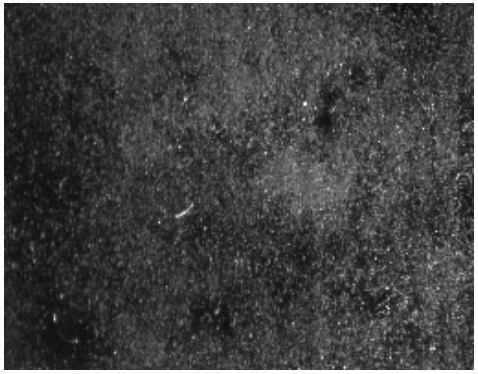


- Utilize LANL's standard ink formulation to compare with previously tested MEAs.
- Prepare MEAs with Hot-Press Decal Transfer Method to start (conventional Pt/C methods).
- Test MEAs in an operating fuel cell using identical test protocol (i.e. H_2/Air flow, Cell Temp, Pressure, and RH).
- Characterize using XRF, cyclic voltammetry, AC impedance, and VI curves.

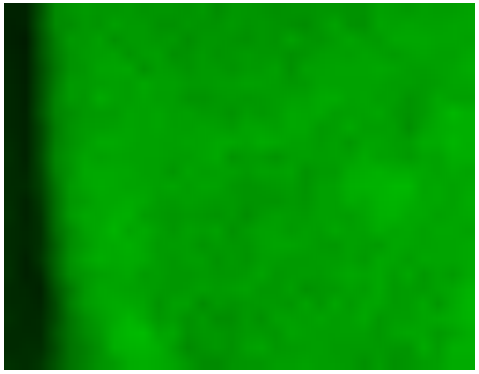
LANL standard hardware

Technical Accomplishments and Progress (FY12): MEA Preparation and Characterization

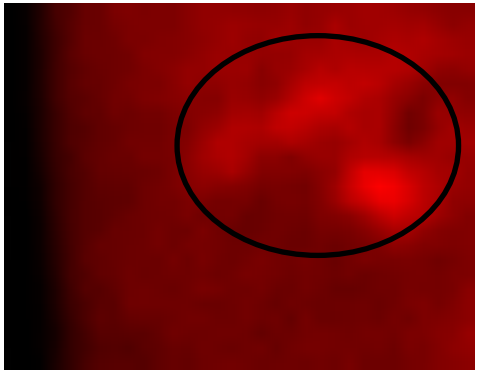
EDAX mapping and X-ray tomography of TiO_2/20%wt Pt ink before Fuel cell testing



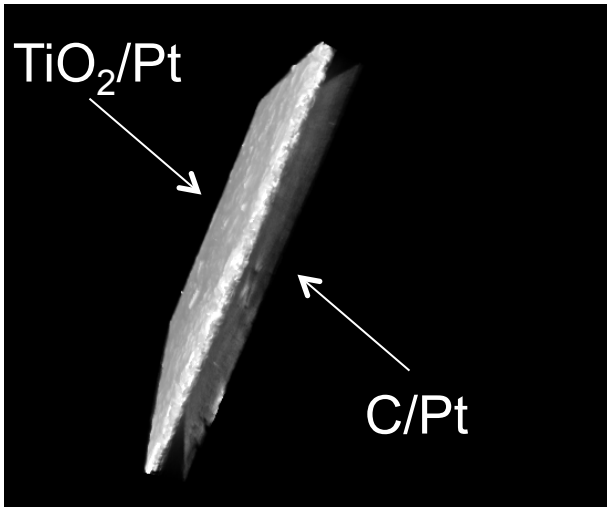
TiO_2/20% Pt

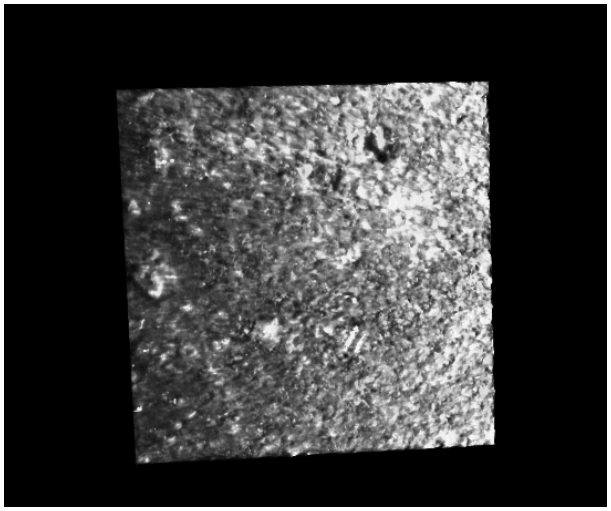


Pt mapping



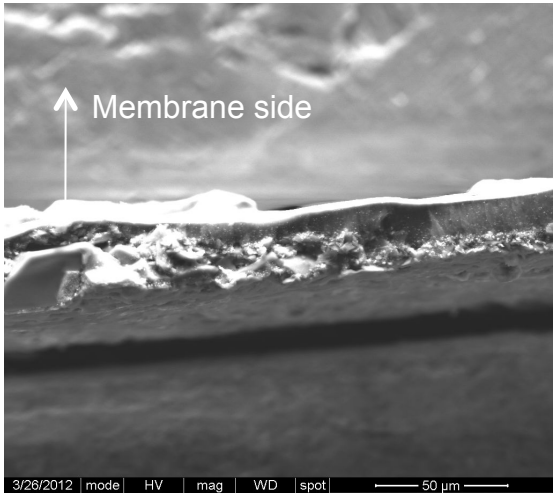
Ti mapping

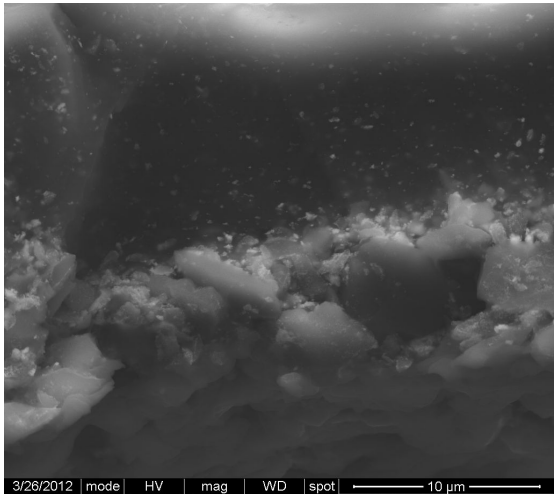


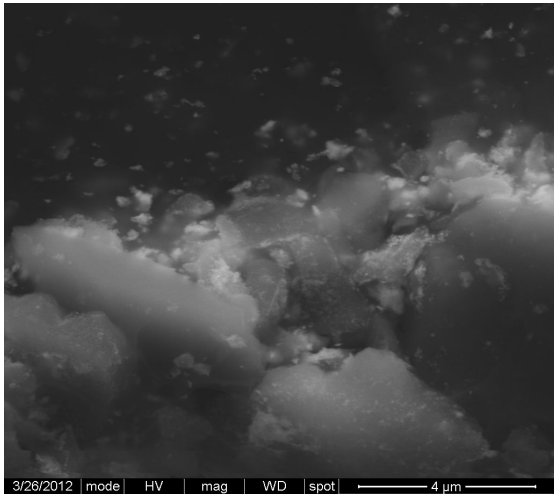


Pt is relatively well distributed, Ti is not well distributed. TiO_2/Pt thickness is relatively high.

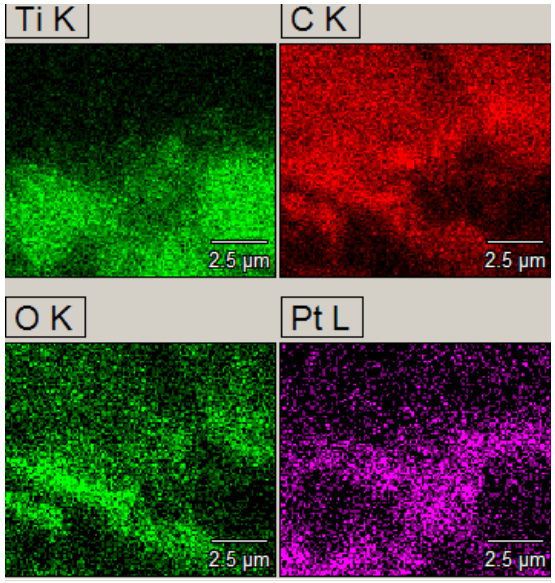
Technical Accomplishments and Progress FY12: SEM of the TiO_2/Pt Layer Cross Section



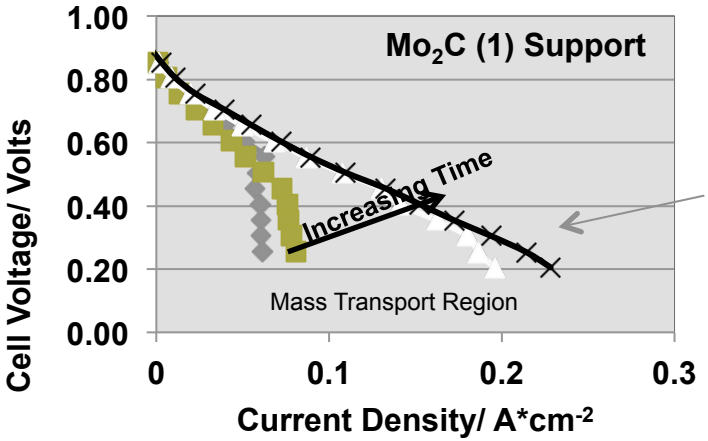




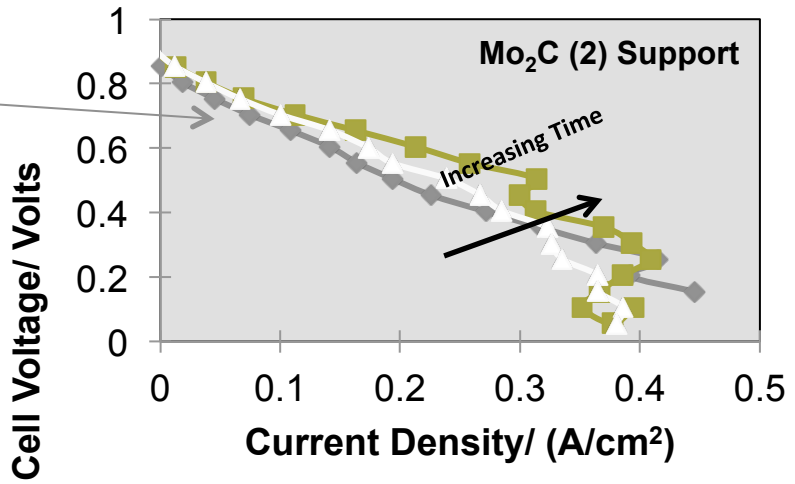
- MEA fabrication needs to be optimized
- Ti tends to separate from the carbon
- Pt seems to favor the Ti over the C
- The loss of carbon can result in the loss of all the support.



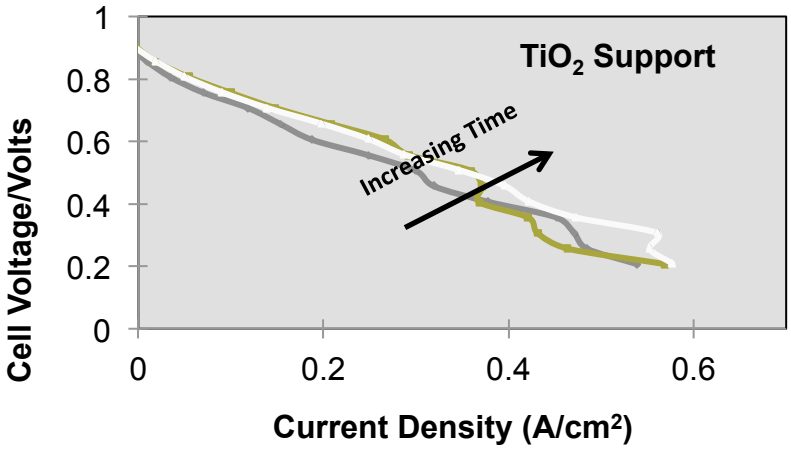
Technical Accomplishments and Progress FY12: Fuel Cell Testing

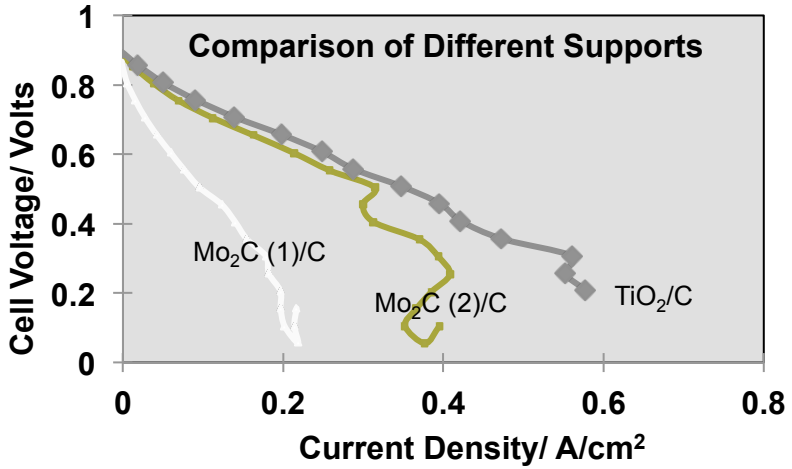


The **Mo_2C** support shows a gradual improvement over time, clearly in the mass transport region **(on the left)**, but better processing lead to an overall increase in performance **(on the right)**.



Further improvements are anticipated through better understanding of support positioning within the electrode.





- The **TiO_2** support shows gains in the **kinetic region**
  - this points toward an increase in catalytic activity (possible through catalyst morphology, i.e. better gas access and/or three phase boundary)
  - and an increases over time along the polarization curve

- 5 cm^2 MEA: 0.2 ± 0.02 mg Pt/cm^2
- Cell Temp: 80°C, 100% RH, Back Pressure: 30 psig ,GDL: SGL 25BC, H_2/Air Flows: 160/550 sccm (fixed)
- VI's taken in ~ 24 hr increments

Proposed Future Work – FY13

- Characterization and testing of support materials (on-going throughout the entire project).
- Send samples to ORNL for TEM characterization.
- Send samples to UNM for XPS characterization.
- Continue fuel cell testing and lifetime-durability observations with Pt/Mo_2N-C (via PAD), Pt/Mo_2N, and TiO_2/C (via PAD).
- Continue durability testing both fuel cell and half cell.
- Optimization of MEA fabrication with ceramic supports.
- High surface area Mo_2N and TiO_{2-x} through aerosol synthesis route at UNM and characterization.
- Publications.

Summary of Technical Progress for FY12

- Electrochemical characterization including emphasis on durability studies has been increased in FY12 and will continue to be primary focus throughout the rest of year.
- Changes to project experimental effort made based on AST and modeling results.
- AST testing show correlation between durability and carbon content in the supports – ceramic supports with least carbon contamination show better durability.
  - New RES-prepared Mo_2C with imbedded Pt shows surprising activity and durability.
- Fuel cell testing started with supports derived from PAD process.
- Return to work on titania supports – put on hold after FY11 Go decision to focus on Mo_2N support – with emphasis on Nb-substituted TiO_2. Ideal for PAD process.
  - Modeling of Ti_4O_7 phase started although calculations suggest that Pt affinity not as good as Pt on defected Mo_2N surface.
- Ink formulation and MEA preparation work done in FY12.
  - Established methods optimized for Pt/C need to be changed for ceramic supports.
- Fuel cell testing started in FY12 with available supports but improvement necessary.

Publications and Presentations

- K.J. Blackmore, E. Bauer, L. Elbaz, E.L. Brosha, T.M. McCleskey, and A.K. Burrell, “Engineered Nano-scale Ceramic Supports for PEM Fuel Cells,” ECS Transactions for 2010 Fuel Cell Seminar, Vol. 30, no. 1, (2010) 83-90.
- K.J. Blackmore, L. Elbaz, E. Bauer, E.L. Brosha, K. More, T.M. McCleskey, and A.K. Burrell, “High Surface Area Nitride Support for Fuel Cell Electrodes,” *J. Electrochem. Soc.* 158, no. 10 (2011) B1255-B1259.
- D.A. Konopka, S. Pylypenko, P. Atanassov, and T.L. Ward, “Synthesis by Spray Pyrolysis of Mesoporous NbRuyOz as Electrocatalyst Supports in Fuel Cells,” *ACS Applied Materials & Interfaces* **2** (1) (2010) 86-95.
- D. Konopka, B. Kiefer, Y.B. Jiang, T. Ward, and P. Atanassov, “Electrochemical and DFT Analysis of Deactivation of Pt Supported on Niobia,” *ECS Transactions* (2010).
- D.A. Konopka, B. Kiefer, Y.B. Jiang, T.L. Ward, and P. Atanassov, “Electrochemical Studies and DFT Analysis of Niobia Passivation of the Pt Surface,” Submitted to *J. Electrochem. Soc.* (2010)
- K. Blackmore, E. Brosha, A. Burrell, L. Elbaz, N. Henson, and K. More, “Alternative Supports for Polymer Electrolyte Fuel Cell Cathodes,” 219th Meeting of the Electrochemical Society, Montreal, CA. May 1-6, 2011.
- K. Blackmore, E. Brosha, A. Burrell, L. Elbaz, N. Henson, and K. More, “Electrochemical study and modeling of Pt-Mo_2N interactions”, in preparation.
- D. A. Konopka, M. Li, K. Artyushkova, N. Marinkovic, K. Sasaki, R. Adzic, T. L. Ward, and P. Atanassov, "Platinum Supported on NbRuyOz as Electrocatalyst for Ethanol Oxidation in Acid and Alkaline Fuel Cells", *J. Phys. Chem C* **115** (7)3043-3056 (2011).
- P. Atanassov, D. Konopka, B. Kiefer, Y. Jiang, and T. Ward, "Electrochemical Studies and DFT Analysis of Pt Stability and Surface Passivation on NbRuyOz Support" , *Journal of The Electrochemical Society*, submitted (2011).
- Lior Elbaz, Karen Blackmore, Anthony Burrell, and Eric Brosha, “Molybdenum Nitride Imbedded with Platinum as Support for Platinum Catalysts for Oxygen Reduction in Fuel Cells,” 2011 Fuel Cell Seminar and Exposition, October 2011.
- Claudia C. Luhrs, Eric Brosha, and Jonathan Phillips, “Method for Generation of Supported Metal Catalysts : Rapid Heating of Physical Mixtures of Urea, Metal Nitrates and Ceramic Oxides, UNM-1067.PRO filed January 2011.
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